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This final report on Grant Number DAAL03-87-K-0132 contains a Statement of Problem Studied, A Summary of Important Results, a list of Publications and Technical Reports Published During Award Period, and a list of Scientific Personnel Supported by the ARO. The work was performed at the Department of Chemistry at the University of Missouri-Columbia.

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FINAL REPORT

"The Redox Chemistry of Some Peroxo and Superoxo Metal Ion Complexes"

Grant Number: DAAL03-87-K-0132

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Statement of Problem Studied

The water - dioxygen cycle is a fundamental yet complex process. Important intermediates often include peroxide and superoxide. It is well established that metal ions can profoundly affect both the rate and the mechanism of this cycle, often in a catalytic manner. We have thoroughly characterized peroxo complexes in aqueous solution in order to probe the mechanistic role played by the metal ion. In effect, we start in the middle of the water - dioxygen cycle with a well defined system. The early transition metals in their highest oxidation states have been used as the metal ions for these studies. These d^0 ions rapidly form robust peroxo and superoxo complexes. We have examined the redox chemistry of these complexes. This chemistry is compared with that of the dioxygen analogues H_2O_2 (or HO_2^-) and HO_2 (or O_2^-) for the purpose of assessing in a detailed manner the role of the metal ion.

In a limited sense these studies are complementary to intensive research efforts by others on such topics as the use of peroxo complexes as oxygen transfer agents in synthesis, the development of singlet oxygen generators, the utilization of dioxygen in biological systems, the search for catalysts for the oxygen electrode component of fuel cells, and decontamination procedures that use hydrogen peroxide as the oxidant.

Summary of Important Results

The reactivity of coordinated peroxide in peroxo complexes is enormously dependent on the identity of the metal ion. We have studied in detail a number of reactions involving oxygen atom transfer from and one-electron reductions of peroxo complexes. For both types of reactions the reactivities vary with the metal center in the order $W(VI) > Mo(VI) \gg Cr(VI) > V(V) > Ti(IV) > Zr(IV)$. The peroxo complexes of $W(VI)$ are ca. 10^4 times more reactive than hydrogen peroxide, whereas the peroxo complexes of $Ti(IV)$ are typically 10^3 times less reactive than hydrogen peroxide. We have devoted considerable effort to elucidating the mechanisms of reactions of these peroxo complexes and to learn why the reactivities are so enormously variable. Conclusions drawn from these studies to date are:

1) The substrate attacks the triangularly coordinated peroxo ligand in an inner-sphere manner for both types of reactions examined - attack at the metal center is unimportant

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under our experimental conditions.

2) Complexes containing only one peroxo ligand or only bridging peroxo ligands appear to be less reactive than hydrogen peroxide.

3) The strong dependence of reactivity on the identity of the metal center is seen in isostructural species. In particular, the relative reactivities of the oxodiperoxo complexes of W(VI), Mo(VI), Cr(VI), and V(V) stand in the listed order and span some four orders of magnitude. These relative reactivities are independent of the substrate - we have examined both reactive and sluggish substrates.

As mentioned, W(VI) and Mo(VI) are especially effective at activating peroxide. The reactions are strictly catalytic with respect to the metal ion provided excess hydrogen peroxide is present. These metal ions form peroxo complexes over nearly the entire pH region, and may find application as catalysts for a number of reactions of the normally sluggish oxidant hydrogen peroxide. We have initiated but not yet completed studies of the peroxo complexes formed by these metal ions in basic solution. It is safe to conclude that in addition to the known tetraperoxo complex, $M(O_2)_4^{2-}$, a triperoxo complex of probable formula $MO(O_2)_3^{2-}$ is of importance (in addition to $MO(OH)(O_2)_2^-$ and $MO_2(O_2)_2^{2-}$). It is a major challenge to identify and determine the equilibria between these peroxo complexes in basic solution, but we have nearly completed the task.

Superoxo complexes appear to be involved as intermediates in one-electron reductions of oxodiperoxo complexes (and perhaps other peroxo complexes as well). This surprising feature results from the initial formation of hydroxyl radical which does not escape the coordination sphere of the metal center but instead oxidizes a peroxo ligand. The superoxo complex does not survive long since it is usually more reactive towards the reductant than is its precursor, the peroxo complex. These results illustrate the point that peroxo and superoxo metal ion complexes probably play very important roles in metal ion mediated reactions of dioxygen.

Molybdate is known to be an effective catalyst for the decomposition of hydrogen peroxide in basic solution. It has recently been shown that the dioxygen product of the decomposition is quantitatively singlet oxygen. Since the reaction consumes no acid or base, it represents perhaps the simplest chemical means known for producing singlet oxygen. We have been able to demonstrate that only one peroxo complex is responsible for this remarkable reaction - the triperoxo complex which we tentatively formulate as $MoO(O_2)_3^{2-}$. We propose that the reason for the unique reactivity of this complex is that one peroxo ligand is unable to bond effectively as a bidentate ligand due to the probable pentagonal bipyramidal geometry - the apical position trans to the oxo ligand is known to bond weakly to bidentate ligands, a situation that would be even more severe for the small peroxo ligand. As a consequence, the pendant, singly bonded ligand can react effectively with a second peroxo ligand. In this picture, the Mo(VI) is acting as a template that positions two peroxo ligands for reaction. This explanation is admittedly speculative, but forms the basis for devising experiments to further elucidate what we consider to be a very important system.

Publications and Technical Reports Published During Award Period

1. "Kinetic Study of the Oxygen Atom Transfer Reactions from the Oxo Diperoxo Complexes of Molybdenum(VI) and Tungsten(VI) to (Thiolato)- and (Sulfenato)cobalt(III) Complexes", Ghiron, A.F.; Thompson, R.C. *Inorg. Chem.* **1988**, 27, 4766.
2. "The Effect of pH on the Redox Reactions of Oxodiperoxomolybdenum(VI)", Thompson, R.C. in *Proceedings of the 1987 U.S. Army CRDEC Scientific Conference on Chemical Defense Research*, CRDEC-SP-88013, **1988**, 709.
3. "Comparative Kinetic Study of Oxygen Atom Transfer Reactions of Oxohydroxodiperoxomolybdenum(VI) and Oxo(oxalato)diperoxomolybdenum(VI) in Aqueous Solution", Ghiron, A.F.; Thompson, R.C. *Inorg. Chem.* **1989**, 28, 3647.
4. "Kinetic Study of the Formation of the Oxo Diperoxo Complexes of Molybdenum(VI) and Tungsten(VI) and Their Reduction by Iron(II), Europium(II), the Methyl Viologen Radical Cation, and the Dithionite Ion", Schwane, L.M.; Thompson, R.C. *Inorg. Chem.* **1989**, 28, 3938.
5. "Kinetic Study of the Formation of the Oxo Diperoxo Complex of Tungsten(VI) in Aqueous Perchloric Acid Solution", Islam, M.A.; Thompson, R.C. *Inorg. Chem.* **1989**, 28, 4419.
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7. "Comparative Kinetic Study of Oxygen Atom Transfer Reactions of Diperoxo and Monoperoxo Complexes of Oxovanadium(V) in Aqueous Solution", Ghiron, A.F.; Thompson, R.C. *Inorg. Chem.* **1990**, 29, 4457.

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